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Bioinspired Surface Treatments for Improved Decontamination: Silicate-Based Slippery Liquid-Infused Porous Surfaces (SLIPS)

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This effort evaluates bioinspired coatings for use in a top-coat type application to identify those technologies that may improve decontamination capabilities for painted surfaces. This report details results for evaluation of a slippery liquid-infused porous surface (SLIPS) based on a porous organosilicate layer. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphate, and diisopropyl fluorophosphates following treatment of contaminated surfaces with a soapy water solution is reported. Wetting behaviors and target droplet diffusion on the surfaces are also discussed.

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EXECUTIVE SUMMARY

The Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) initiated a program in January 2015 for evaluation of bioinspired treatments suitable for use as a top coat on painted surfaces with the intention of achieving improved aqueous decontamination of these materials. Funding was provided by the Defense Threat Reduction Agency (DTRA, CB10125). This report details results for evaluation of a slippery liquid-infused porous surface (SLIPS) based on a porous organosilicate layer. Two variants were evaluated on a glass support, one including only methyl groups and the other incorporating both methyl and fluorinated groups. Several lubricating oils were also evaluated, four silicone based oils and Fomblin Y. On polyurethane paint coated aluminum coupons, the organosilicate layer of methyl and fluorinated groups was lubricated with Fomblin Y or one of two silicone based oils. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphate, and diisopropyl fluorophosphate following treatment of contaminated surfaces with a soapy water solution is reported along with droplet diffusion on the surfaces and wetting angles.

BIOINSPIRED SURFACE TREATMENTS FOR IMPROVED DECONTAMINATION: SILICATE-BASED SLIPPERY LIQUID-INFUSED POROUS SURFACES (SLIPS)

INTRODUCTION

The DoD Chemical and Biological Defense Program (CBDP) seeks to provide protection of forces in a contaminated environment including contamination avoidance, individual protection, collective protection, and decontamination. In January 2015, the Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) began an effort funded through the Defense Threat Reduction Agency (DTRA, CB10125) with a view toward evaluation and development of top-coat type treatments suitable for application to painted surfaces that would reduce retention of chemical threat agents following standard decontamination approaches. The effort sought to survey relevant and related areas of research and evaluate identified technologies under appropriate methods to determine efficacy, scalability, and durability.

The current document summarizes results for one of the identified technologies. In this case, a slippery liquid-infused porous surface (SLIPS). Slippery liquid-infused porous surfaces (SLIPS) comprise a film of lubricating liquid with a textured substrate (micro/nano or both). [1-4] This provides a surface that is effectively smooth on the molecular scale and a liquid-liquid interaction interface. This is in contrast to the commonly harnessed lotus leaf effect that is achieved through use of a textured surface providing air-liquid and air-solid interfaces. In addition, SLIPS offers a self-healing mechanism for damage to the surfaces, especially damage with a long, narrow surface profile. The liquid lubricant of the SLIPS treatment will flow to fill the region of damage, maintaining the overall liquid-liquid surface interactions. The solid and liquid components of a SLIPS system are selected to repel liquids of interest.

The silicate-based SLIPS treatment used under this study uses a surfactant-templated nanoporous organosilicate modified with methyl and nonafluorohexyl groups to provide the functionalized textured surface. The coating is deposited and extracted or left as synthesized to provide empty pores or pores filled with the surfactant template, respectively. Finally the surface is infused with an oil typically Fomblin® Y, a perfluoropolyether (PFPE), though the similar Krytox oils and even silicone based oils can be used. For the complete system, aluminum coupons painted with a polyurethane paint system were treated with the porous silicate layer by spin-coating. They were subsequently lubricated with an oil (Figure 1). The coupons were subjected to standard evaluations including measurement of sessile, sliding, and shedding contact angles and quantification of retention for the simulant compounds.

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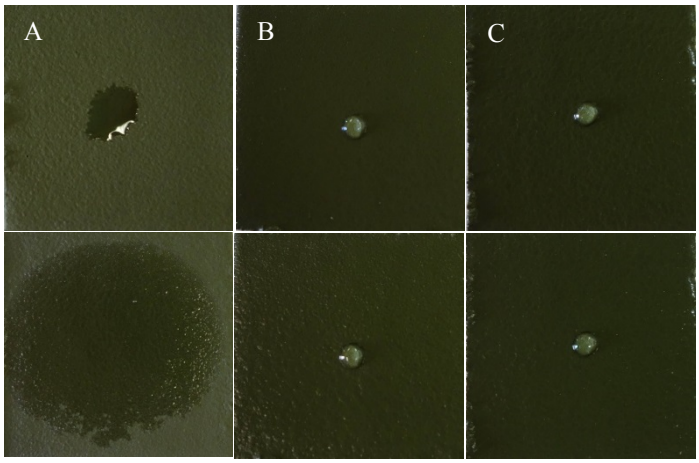

Fig. 1 — Images of a painted coupon (A), the as synthesized SLIPS treatment (B), and the extracted SLIPS treatment (C) with a standing droplet methyl salicylate immediately following liquid application (top) and 5 min after liquid application (bottom).

METHODS

Originally, methylsilicate-based SLIPS with no fluorinated functional groups were synthesized and tested. Methylsilicate $ARSiO_2$ SLIPS surfaces were synthesized by adapting a component of a process described in a paper focused on anti-reflective (AR) and self-cleaning coatings for photovoltaic cells. [5] In a 120 mL PTFE jar, a mixture of 0.05 g 2M HCl, 1.69 g H_2O, 2 g tetraethyl orthosilicate, 1.71 g methyltriethoxysilane (MTS), and 35.38 g ethanol was stirred at room temperature. 1.45 g Pluronic F127 was added and the sol mixture was stirred for more than 2 h at room temperature. The sol was used to spin-cast films on ethanol rinsed No. 1 ½ cover glass substrates at 500 RPM for 30 s. MSS films were cured in an oven with the temperature increased 1°C/min from room temperature to 100°C where it was held for 6 h. The MSS films were soaked in ethanol at 65°C for 1 d to extract F127. The transparent and crack-free extracted samples were rinsed with ethanol and dried at 65°C. One sample was broken up and subjected to nitrogen adsorption characterization (Figure 2). The MSS film on glass (with glass substrate contributing the vast majority of mass and screening the measured surface area of the film) yielded a small type IV-like mesoporous feature in its nitrogen adsorption-desorption isotherm, a BET surface area of 1.34 m^2/g, and a single point total pore volume of 0.00577 cm^3/g. Different lubricating oils were compared on these coated glass samples: silicone oil AR20 (viscosity ~ 20 mPa. s, Aldrich), silicone oil AR200 (viscosity ~ 200 mPa. s, Aldrich), dimethylpolysiloxane (viscosity 20 cSt, Sigma), and dimethylpolysiloxane (viscosity 500 cSt, Sigma). Note that the "AR" designation on some silicone oils has no relation to the overarching "AR" nomenclature for these anti-reflective top-coat materials).

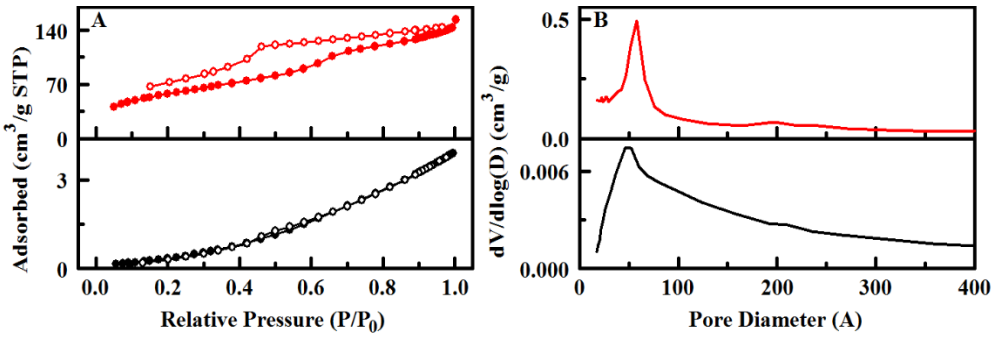

Fig. 2 — Nitrogen adsorption / desorption data (A) and pore size distributions (B) for the MSS samples: thin film (black) and bulk (red).

A first attempt to incorporate fluorinated groups into the type of coating described above replaced the 1.71 g MTS with 3.94 g nonafluorohexyltriethoxysilane (NFHS), an equimolar amount (0.0096 mol). The ethanol-extracted $ARSiO_2$-F film did not display evidence of porosity when a sample was characterized by nitrogen adsorption. Additional materials incorporating fluorinated groups, $ARSiO_2$-MF and $ARSiO_2$-MF2, were prepared by combining the organosilane precursors to provide both methyl and fluoroalkyl groups. $ARSiO_2$-MF sol was prepared in a 120 mL PTFE jar by stirring a mixture of 0.05 g 2M HCl, 1.69 g H_2O, 2 g tetraethyl orthosilicate, 1.28 g MTS (0.0072 mol), 0.99 g NFHS (0.0024 mol), and 35.38 g ethanol at RT. 1.45 g Pluronic F127 was added and the sol was stirred >2 h at room temperature. The sol was used to cast films as described above. Handling, curing, and extraction were completed as described for the methylsilicate $ArSiO_2$ SLIPS materials. One sample was broken up and subjected to nitrogen adsorption characterization (Figure 3). A BET surface area of 2.91 m^2/g and single point total pore volume of 0.0126 cm^3/g were measured.

The fluoroalkyl groups were further increased in the $ARSiO_2$-MF2 material (MFSS) through doubling the incorporated NFHS. In a 120 mL PTFE jar, a mixture of 0.05 g 2M HCl, 1.69 g H_2O, 2 g tetraethyl orthosilicate, 0.86 g MTS (0.0048 mol), 1.97 g NFHS (0.0048 mol), and 35.38 g ethanol was stirred at RT. 1.45 g Pluronic F127 was added and the sol was stirred >2 h at RT. The sol was used to spin-cast films on ethanol rinsed No. 1 ½ cover glass substrates at 500 RPM for 30 s. A "bulk" material was also prepared by dropping some of the sol into a plastic culture dish. MFSS films and bulk material were cured in an oven; temperature was increased 1°C/min to 100 °C and held for 6 h. Here, some of the film samples and all of the bulk product were extracted using the ethanol process. The transparent and crack-free extracted MFSS samples (bulk material was in pieces) were rinsed with ethanol and dried at 65°C. Nitrogen adsorption characterization of a crushed, extracted film sample determined a BET surface area of 3.87 m^2/g and single point total pore volume of 0.0119 cm^3/g (Figure 3). Bulk material yielded a type IV mesoporous isotherm with significant hysteresis between the adsorption and desorption branches, with a BET surface area of 115 m^2/g, single point total pore volume of 0.158 cm^3/g, and a BJH adsorption pore size distribution peak ca. 74 Å (Figure 3). Samples of both extracted and as-synthesized (F127 not extracted in ethanol) MFSS films were infused with Fomblin Y fluorinated liquid.

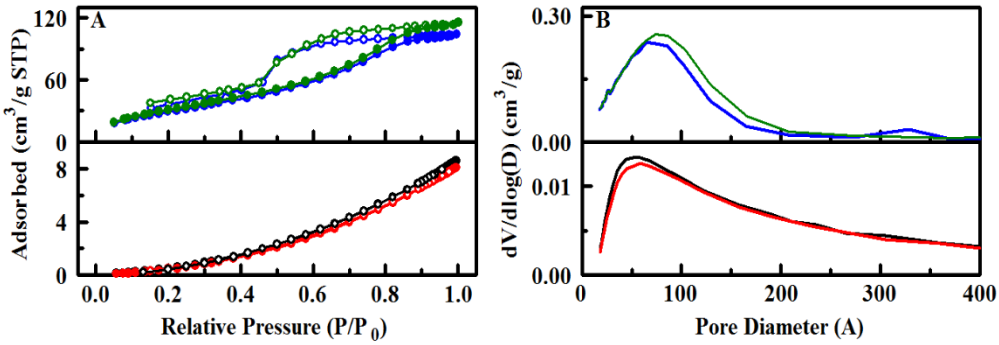

Fig. 3 — Nitrogen adsorption / desorption data (A) and pore size distributions (B) for the fluorinated samples: $ARSiO_2$-MF thin film (black), MFSS thin film (red), two examples of MFSS from bulk synthesis (green and blue).

MFSS coatings were deposited on aluminum coupons coated with a polyurethane paint system. Coupons were rinsed first with ethanol while spinning at 500 RPM. MFSS sol (prepared as described above) was spin-cast on coupons at 500 RPM for 30 s; sol was also dropped into a culture dish to obtain bulk product for quality control evaluation. Coated coupons and bulk material were cured in an oven; temperature was increased 1°C/min to 100°C and held for 6 h. Part of the resulting coupons were soaked in ethanol at 65°C for 2 d to extract F127 while others were held in reserve and not extracted. Extracted materials were rinsed with ethanol and dried at 65°C. Nitrogen adsorption characterization of extracted bulk material measured a BET surface area of 122 m^2/g, single point total pore volume of 0.174 cm^3/g, and BJH adsorption pore distribution peak ca. 74 Å; these values and the isotherm shape closely matched those observed from the previous experiments. Samples of both extracted and as-synthesized MFSS coatings on painted surfaces were infused with the Fomblin Y fluorinated liquid.

Sessile contact angles for samples evaluated under this effort used three 3 µL droplets per surface with each droplet measured independently three times for each of three targets, water, ethylene glycol, and n-heptane. Geometric surface energy was calculated based on the water and ethylene glycol interactions using software designed for the DROPimage goniometer package. Sliding angles were determined using 5 µL droplets. The droplet was applied at 0° after which the supporting platform angle was gradually increased up to 60°. Sliding angles for each of the liquids were identified as the angle for which movement of the droplet was identified. Shedding angles for each liquid were determined using 12 µL droplets initiated 2.5 cm above the coupon surface. Changes in base angle of 10° were utilized to identify the range of droplet shedding angle based on a complete lack of droplet retention by the surface (not sliding). The angle was then reduced in steps of 1° to identify the minimum required angle. Droplet diameters were determined using tools provided by Adobe Photoshop CS3. Droplets of 5 mL were applied to the surfaces and images were collected at 30 s intervals for 5 min followed by images at 5 min intervals for a total of 30 min. DFP samples were kept covered for the duration of the experiment to minimize evaporation. In some cases, reflections from the glass cover can be seen in the images.

Simulant exposure and evaluation methods were based on the tests developed by Edgewood Chemical Biological Center referred to as Chemical Agent Resistance Method (CARM). [6] Standard target exposures utilized a challenge level of 10 g/m^2. The glass coupons were 0.00188 m^2; the 10 g/m^2 target challenge was applied to the surfaces as four equally sized neat droplets. The painted coupons were 0.00101 m^2; the 10 g/m^2 target challenge was applied to the surfaces as two equally sized neat droplets. Following application of the target, coupons were aged 1 h prior to use of a gentle stream of air to expel target from the surface. Samples were then rinsed with soapy water (0.59 g/L Alconox in deionized water) The rinsed

coupons were soaked in isopropanol for 30 min to extract remaining target; this isopropanol extract was analyzed by the appropriate chromatography method to determine target retention on the surface.

For paraoxon analysis, a Shimadzu High Performance Liquid Chromatography (HPLC) system with dual-plunger parallel flow solvent delivery modules (LC-20AD) and an auto-sampler (SIL-20AC; 40 μL injection volume) coupled to a photodiode array detector (SPD-M20A; 277 nm) was used. The stationary phase was a C18 stainless steel analytical column (Luna, 150 mm x 4.6 mm, 3 μm diameter; Phenomenex, Torrance, CA) with an isocratic 45:55 acetonitrile: 1% aqueous acetic acid mobile phase (1.2 mL/min). [7] For analysis of methyl salicylate (MES), diisopropyl fluorophosphate (DFP), and dimethyl methylphosphonate (DMMP), gas chromatography-mass spectrometry (GC-MS) was accomplished using a Shimadzu GCMS-QP2010 with AOC-20 auto-injector equipped with a Restex Rtx-5 (30 m x 0.25 mm ID x 0.25 μm df) cross bond 5% diphenyl 95% dimethyl polysiloxane column. A GC injection temperature of 200°C was used with a 1:1 split ratio at a flow rate of 3.6 mL/min at 69.4 kPa. The oven gradient ramped from 50°C (1 min hold time) to 180°C at 15°C/min and then to 300°C at 20°C/min where it was held for 5 min.

RESULTS

Analysis of the support surfaces (glass, painted aluminum) in the absence of additional coatings provides a point of comparison for evaluating the benefits of the surface treatments. Each table includes data on the relevant support material. Glass only coupons that were rinsed with soapy water prior to extraction retained low levels of all targets, a reflection of the lack of texture on these surfaces. For paint only coupons, retention was significantly higher but was less than that of paint only coupons that were extracted with no rinsing. Though the nominal target application was 10 g/m^2, recovery from surfaces was always less than this value. Losses due to evaporation would be expected, especially for DFP. Additional losses likely occur during rinse steps due to agent interaction with the untreated region of the coupon; the back of these coupons is unpainted aluminum.

Glass Surfaces.

The extracted MSS SLIPS coating was synthesized on a cover glass substrate. Contact angles for material lubricated using four different silicone based oils was compared to that of the glass substrate alone. As shown in Table 1, contact angles for water and ethylene glycol are significantly increased for the SLIPS materials over those observed on glass. The calculated surface energy decreases with increasing viscosity in the lubricating oil. Sliding and shedding angles do not correlate with the viscosity or density of the lubricating oil used. The MFSS SLIPS coating deposited on a cover glass substrate yielded slightly higher contact angles than the MSS SLIPS coatings. Extracted samples yielded higher contact angles than as synthesized variants, and samples lubricated with Fomblin Y yielded higher contact angles than unlubricated variants. The fluorinated coating (MFSS) yielded heptane contact angles between 20° and 30°; glass substrates and methyl only coatings (MSS) were fully wetted by heptane.

The coupons were subjected to simulant exposure, aging, washing, and drying. When the soapy water process was employed on the coated surfaces (Table 2), retention of all targets was low, with the exception of MES on the silicone based oils. While the retention by the MFSS samples here was 2 to 3 orders of magnitude less than that applied, retention of targets by the glass support material is also very low. The smooth nature of the glass support makes for highly homogenous and consistent coatings. Application of this type of coating on the roughness of a painted surface is evaluated in the next section.

Table 1 – Sessile, Sliding, and Shedding Contact Angles on Glass Supports

Coupon	Liquid	Sessile Angle	Sliding Angle	Shedding Angle	Geometric Surface Energy (mJ/m^2)
Glass Support					
Glass Only	water	36.8 ± 0.29	>60	>60	59.1 ± 0.2
	ethylene glycol	26.3 ± 0.1	>60	>60	
	n-heptane	--	>60	>60	
As synthesized MFSS – Fomblin Y	water	102.6 ± 0.4	46 ± 4.1	28 ± 3.0	16.0 ± 0.6
	ethylene glycol	90.9 ± 0.2	47 ± 3.8	15 ± 4.0	
	n-heptane	30.3 ± 0.5	>60	>60	
Extracted MFSS – Fomblin Y	water	115.1 ± 0.1	>60	15 ± 4.0	11.7 ± 0.1
	ethylene glycol	92.7 ± 0.5	>60	20 ± 4.0	
	n-heptane	26.2 ± 0.6	>60	>60	
As synthesized MFSS – no oil	water	104.3 ± 0.5	>60	>60	13.4 ± 0.6
	ethylene glycol	87.9 ± 0.9	>60	>60	
	n-heptane	27.1 ± 0.3	>60	>60	
Extracted MFSS – no oil	water	108.1 ± 0.3	>60	>60	9.4 ± 0.1
	ethylene glycol	96.6 ± 0.3	>60	>60	
	n-heptane	20.9 ± 0.4	>60	>60	
Extracted MSS – silicone oil AR20	water	93.6 ± .02	>60	13 ± 4.0	48.8 ± 2.7
	ethylene glycol	52.7 ± 1.5	30 ± 3.0	13 ± 4.0	
	n-heptane	--	--	--	
Extracted MSS – dimethylpolysiloxane viscosity 20 ost	water	95.9 ± 0.5	>60	>60	40.0 ± 1.0
	ethylene glycol	60.2 ± 0.3	>60	>60	
	n-heptane	--	--	--	
Extracted MSS – silicone oil AR200	water	102.3 ± 0.5	30 ± 2.8	15 ± 4.0	27.2 ± 0.7
	ethylene glycol	74.0 ± 0.2	30 ± 4.1	15 ± 2.0	
	n-heptane	--	--	--	
Extracted MSS – dimethylpolysiloxane viscosity 500 ost	water	98.8 ± 0.6	>60	15 ± 4.1	24.3 ± 1.0
	ethylene glycol	73.2 ± 0.6	>60	20 ± 3.6	
	n-heptane	--	--	--	

Table 2 – Target Retention (g/m^2) Following 1 h Aging on Glass Supports

Coupon	Paraoxon	MES	DMMP	DFP
Glass Support				
Glass Only	0.17	0.22	0.00	0.03
As synthesized MFSS – Fomblin Y	0.09	0.55	0.02	0.10
Extracted MFSS – Fomblin Y	0.39	0.02	0.07	0.23
Extracted MSS – silicone oil AR20	0.15	0.91	ND	0.27
Extracted MSS – dimethylpolysiloxane viscosity 20 ost	0.13	0.09	ND	0.47
Extracted MSS – silicone oil AR200	0.13	2.00	0.01	2.41
Extracted MSS – dimethylpolysiloxane viscosity 500 ost	0.08	0.32	ND	0.67

Aluminum Surfaces.

Both extracted and as synthesized versions of the MFSS coating were applied to painted aluminum coupons. The materials were left unlubricated or lubricated with Fomblin Y. As shown in Table 3 (also Figure 4), application of the MFSS coatings in either the extracted or as synthesized approaches lead to significant increases in wetting angles and decreases in surface energy. The coatings also increase shedding of water and ethylene glycol with angles between 25 and 40°. There are no significant differences between the extracted and as synthesized Fomblin Y oiled coupons. Also shown in Table 3 are values obtained for a paint only coupon that has been oiled with Fomblin Y. While this does not produce the same changes to contact angle as the SLIPS coatings, it does increase the water contact angle and that for heptane. In fact, the heptane angle is larger than that noted for the SLIPS surfaces, and heptane sheds from the oiled surface where it does not from the SLIPS materials.

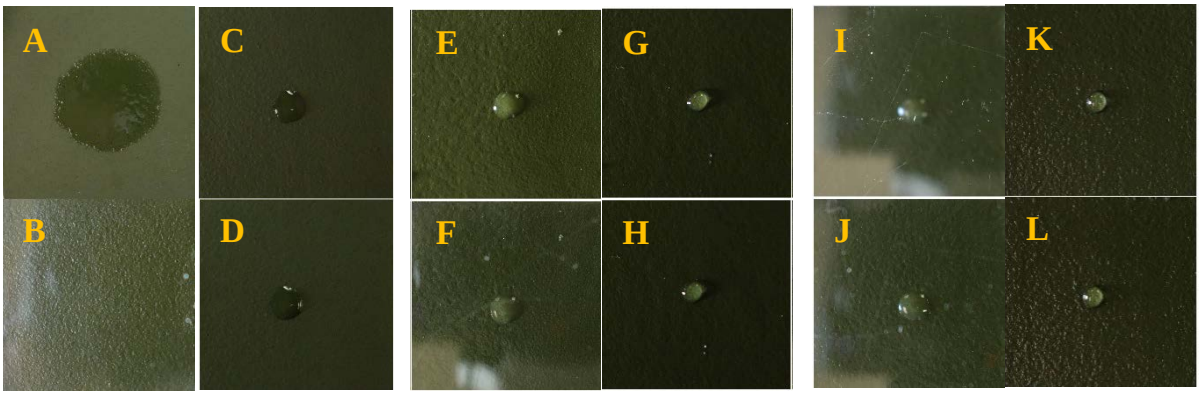

Fig. 4 — Images of a painted coupon and painted coupons treated with the SLIPS formulations with standing droplets of DFP and DMMP: painted coupon with DFP immediately following application (A) and at 30 min (B) as well as those images for a DMMP droplet (C, D); as synthesized SLIPS with DFP immediately following application (E) and at 30 min (F) as well as those images for DMMP (G, H); extracted SLIPS coating with DFP immediately following application (I) and at 30 min (J) as well as those images for DMMP (K, L).

The tendency of droplets to spread across the surfaces was also evaluated (Figure 4; Appendix A). For these studies, droplets of the simulants (5 μL) were utilized. The spread of the droplets was quantified by measuring the diameter of the droplets in the images over time (Figure 5). For the paint only samples, MES and DFP spread quickly reaching the edges of the coupon at 10 and 2 min, respectively. DMMP does not spread during the course of the 30 min incubation. There is very little spread of droplets on either of the Fomblin Y lubricated SLIPS surfaces over the 30 min incubation.

Table 3 – Sessile, Sliding, and Shedding Contact Angles on Aluminum Supports

Coupon	Liquid	Sessile Angle	Sliding Angle	Shedding Angle	Geometric Surface Energy (mJ/m^2)
Aluminum Support					
Paint Only	water	47.5 ± 1.1	>60	>60	71.9 ± 5.1
	ethylene glycol	55.7 ± 2.1	>60	>60	
	n-heptane	--	>60	>60	
Oiled Paint	water	73.1 ± 2.1	>60	46.7 ± 3.3	32.2 ± 1.6
	ethylene glycol	52.5 ± 0.61	>60	49.8 ± 4.9	
	n-heptane	40.1 ± 2.9	>60	36.6 ± 3.3	
As synthesized MFSS – Fomblin Y	water	110.2 ± 0.5	>60	38.3 ± 2.5	13.9 ± 0.9
	ethylene glycol	91.0 ± 0.7	>60	27.5 ± 1.1	
	n-heptane	29.5 ± 1.1	>60	>60	
Extracted MFSS – Fomblin Y	water	111.0 ± 0.9	>60	32.0 ± 6.4	12.0 ± 0.8
	ethylene glycol	93.7 ± 0.8	>60	33.0 ± 5.8	
	n-heptane	26.4 ± 1.6	>60	>60	
Extracted MFSS – no oil	water	114.3 ± 0.66	>60	48.8 ± 0.96	17.3 ± 1.6
	ethylene glycol	89.1 ± 1.3	>60	>60	
	n-heptane	20.6 ± 1.3			
As synthesized MFSS – no oil	water	117.1 ± 1.3	>60	46.8 ± 0.50	20.0 ± 2.1
	ethylene glycol	93.2 ± 0.51	>60	>60	
	n-heptane	22.0 ± 1.6			

The coupons were subjected to several cycles of simulant exposure (10 g/m^2), aging, washing, drying, and lubrication over a period of several weeks. No significant changes in the appearance or wetting characteristics were noted during this period. When the soapy water process was employed (Figure 6; Table 4), retention of all targets was less for the Fomblin Y lubricated SLIPS treatments than for the paint only surfaces. The extracted variant of the MFSS treatment retained less of all targets than the as synthesized treatment. The silicone oil lubrication of the MFSS treatment resulted in greater paraoxon and DMMP retention than that observed for the Fomblin Y lubricated samples. It is important to note that retention of targets by unlubricated variants of these coatings was similar or even lower than that observed for the Fomblin Y lubricated variants.

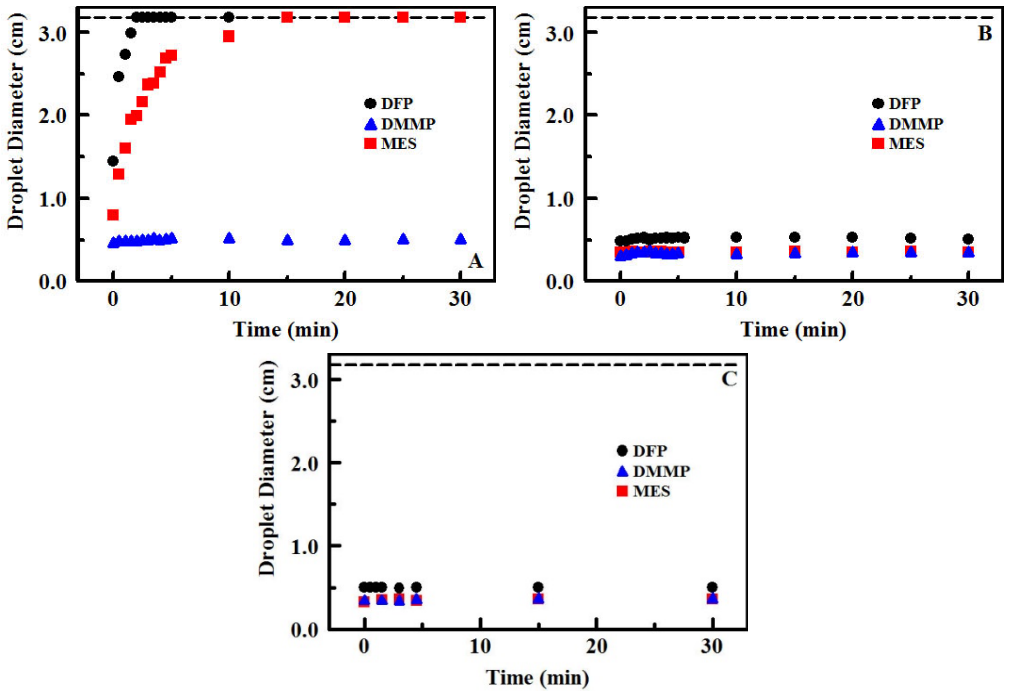

Fig. 5 — Progression of simulant droplet diameters during incubation on the surfaces for DFP (black), DMMP (blue), and MES (red): paint only (A), as synthesized SLIPS lubricated with Fomblin Y (B), and extracted SLIPS lubricated with Fomblin Y (C).

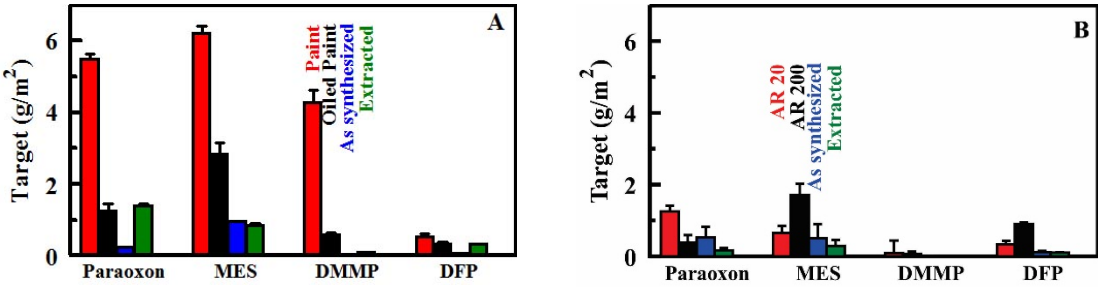

Fig. 6 — Target retention by coupons following treatment with an air stream and rinsing with soapy water: (A) painted coupon (red); Fomblin Y oiled coupon (black); Fomblin Y lubricated, as synthesized SLIPS (blue); Fomblin Y lubricated, extracted SLIPS (green). (B) Extracted coupon lubricated with silicone oil AR 20 (red); extracted coupon lubricated with silicone oil AR 200 (black); unlubricated, as synthesized coupon (blue); unlubricated, extracted coupon (green).

Table 4 – Target Retention (g/m^2) Following 1 h Aging on Aluminum Supports

Coupon	Paraoxon	MES	DMMP	DFP
Aluminum Support				
Paint Only	5.48	6.20	4.28	0.52
Oiled Paint	1.24	2.85	0.59	0.34
As synthesized MFSS – Fomblin Y	0.31	1.88	0.17	0.08
Extracted MFSS – Fomblin Y	0.23	0.98	0.04	0.06
As synthesized MFSS – silicone oil AR20	1.41	0.86	0.10	0.34
Extracted MFSS – silicone oil AR20	1.25	0.65	0.09	0.33
As synthesized MFSS – silicone oil AR200	0.44	0.84	0.08	0.46
Extracted MFSS – silicone oil AR200	0.39	1.71	0.07	0.90
As synthesized MFSS – no oil	0.52	0.50	0.07	0.12
Extracted MFSS – no oil	0.17	0.29	ND	0.10

ND = not detected

CONCLUSIONS

These samples provide promising results with target retention similar to the best samples evaluated to date. The samples also offer low surface energy and target does not spread on the surfaces. Application of the lubricated coating produces a slightly wet look on the painted surfaces (Figure 4 and Appendix). The unlubricated coatings cannot be visually discriminated from the paint alone (Figure 7). Spectrophotometric analysis is necessary to determine the overall impact on color and reflectivity. The long term stability of the coatings should be more thoroughly evaluated.

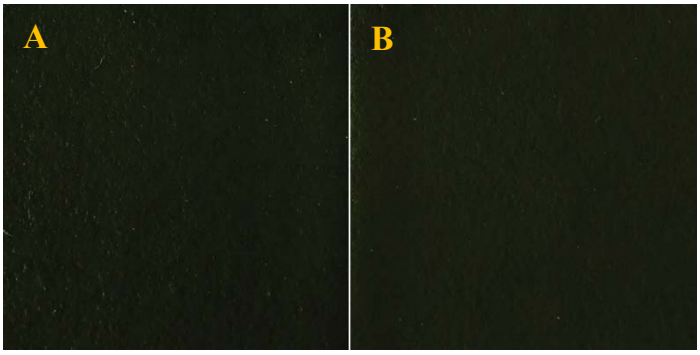

Fig. 7 — Images of painted coupons treated with the extract (A) and as synthesized (B) MFSS coatings in the absence of lubricating oil.

This effort is also evaluating the potential of a covalently attached liquid for addressing the ongoing depletion of the lubricating layer faced by all SLIPS coatings. [8] Though the surface functionalization and

lubricating liquids are tailored to provide favorable interactions between the surface and liquid, there is slow, continual loss at the edges of a coated region as well as during interactions with other liquids (rinsing, for example). At some point, there is no longer sufficient lubricant remaining on the material to provide the desired liquid-liquid surface interface. These lubricating liquids can also be transferred to clothing and skin, presenting a further problem for implementation as a surface treatment for threat agent resistance. The use of a covalently attached liquid could address this shortfall, though it may also impact the self-healing nature of the SLIPS coating.

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Appendix

COUPON IMAGES

Fig. A1 — DFP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 10 (L), 15 (M), 20 (N), 25 (O), and 30 (P) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

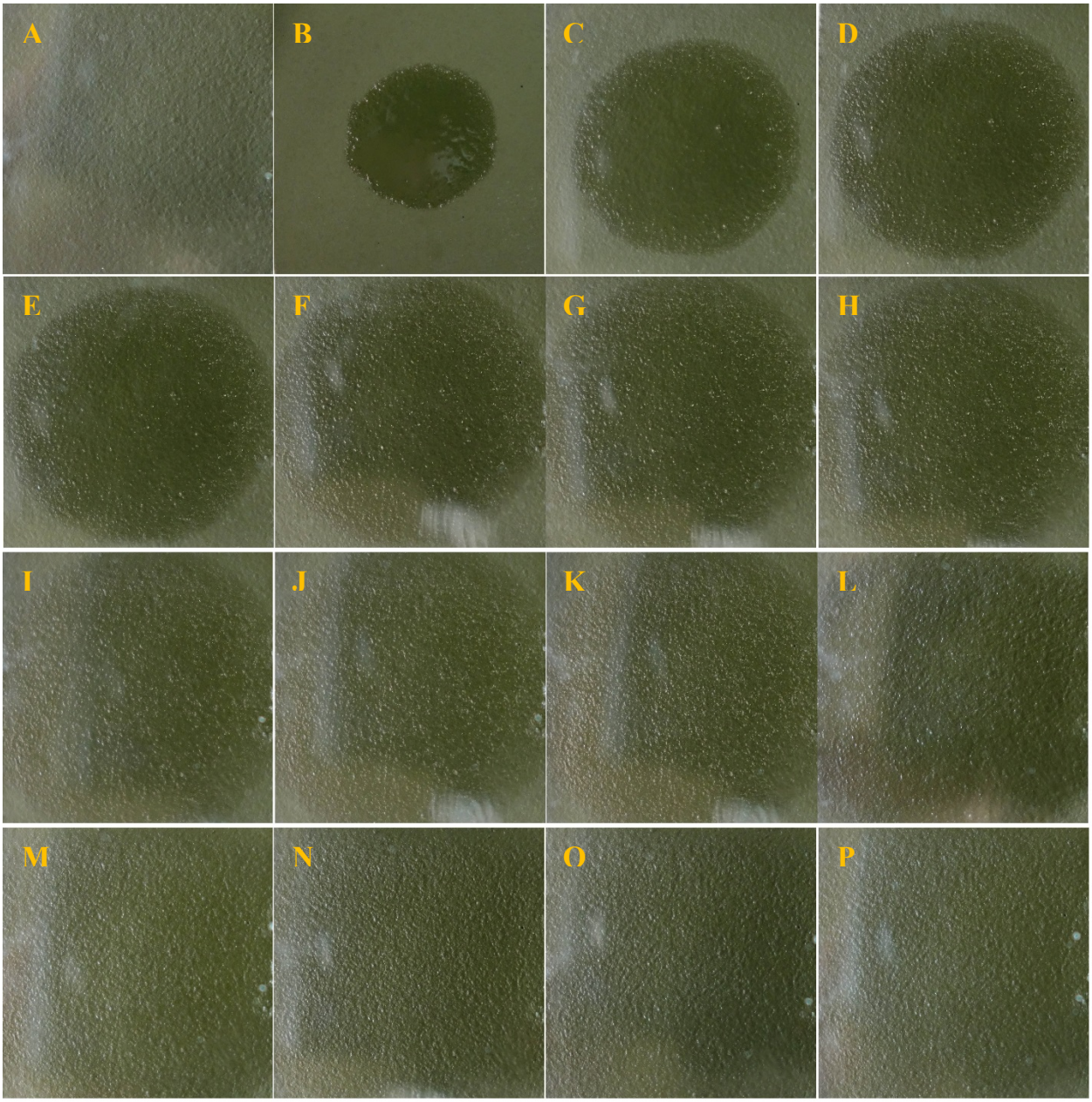

Fig. A2 — MES on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

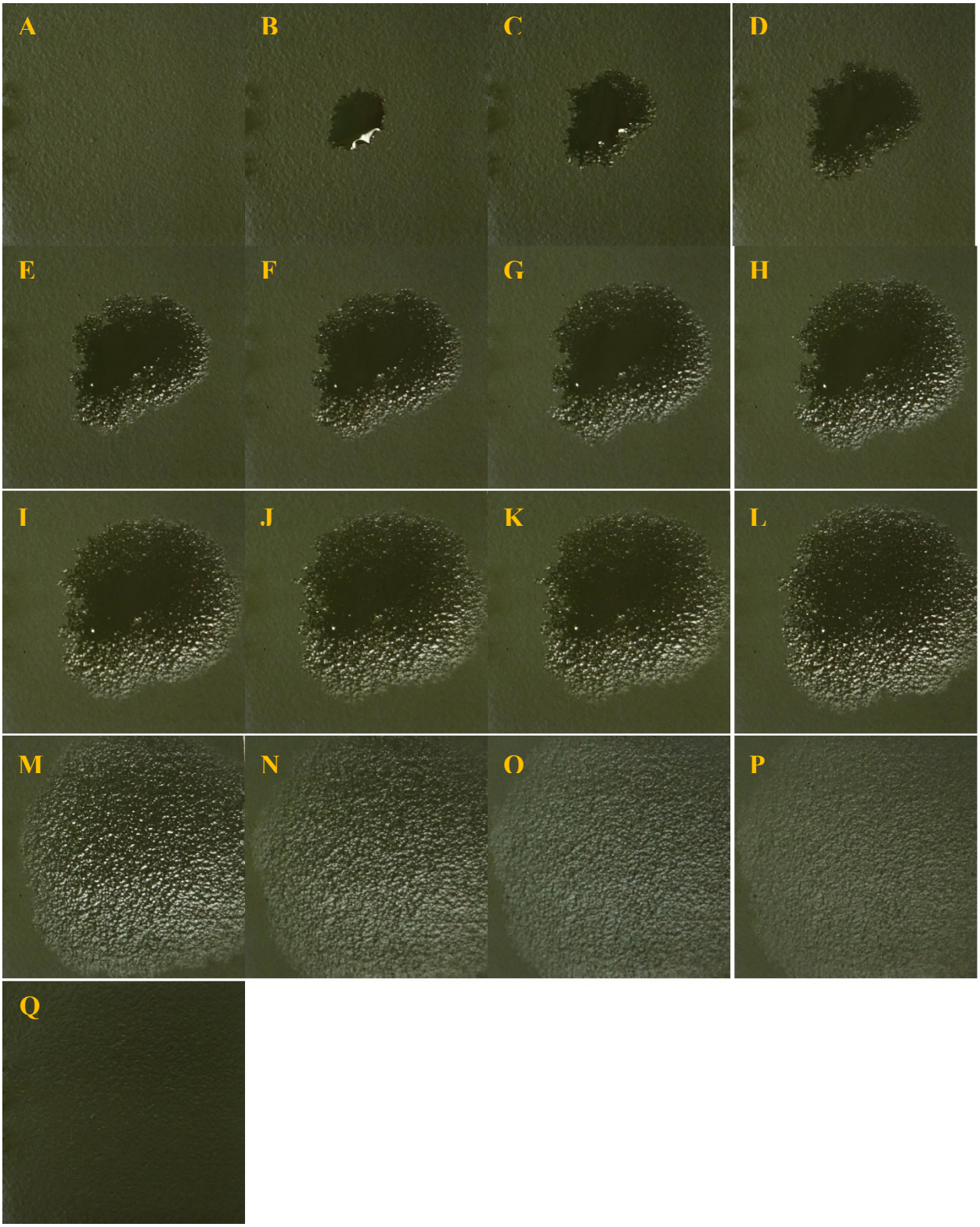

Fig. A3 — DMMP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

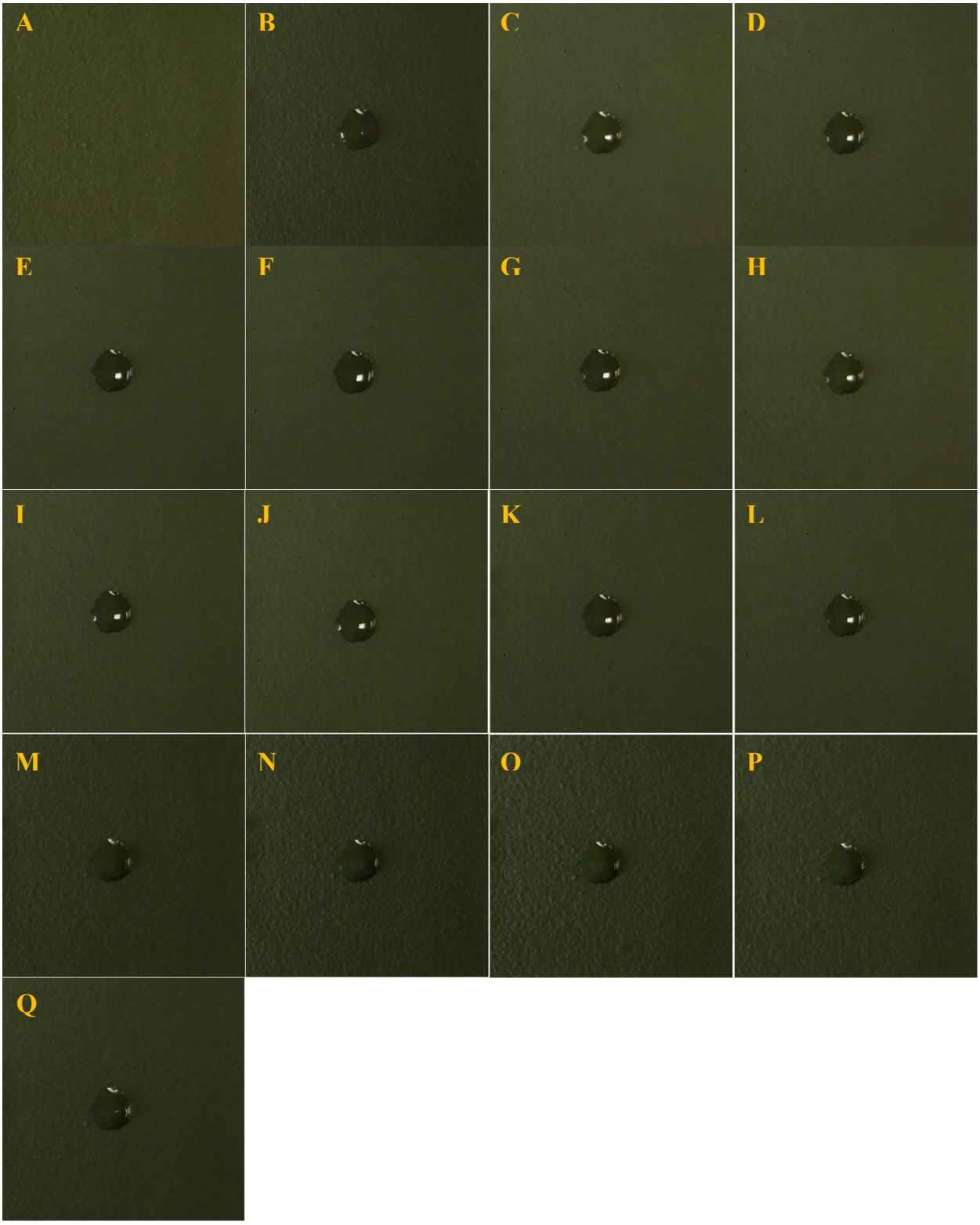

Fig. A4 — DFP on the as synthesized SLIPS coating lubricated with Fomblin Y. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

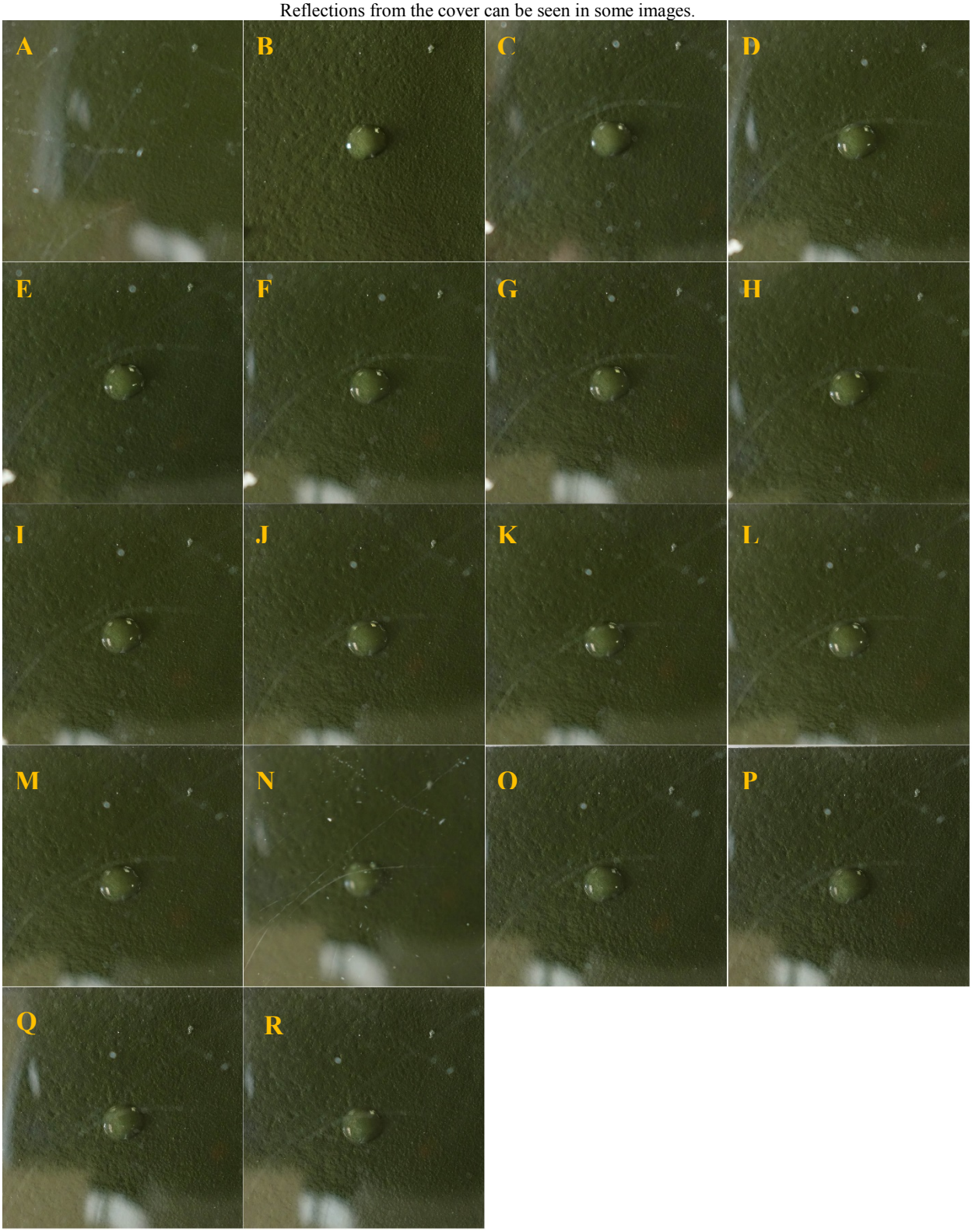

Fig. A5 — MES on the as synthesized SLIPS coating lubricated with Fomblin Y. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

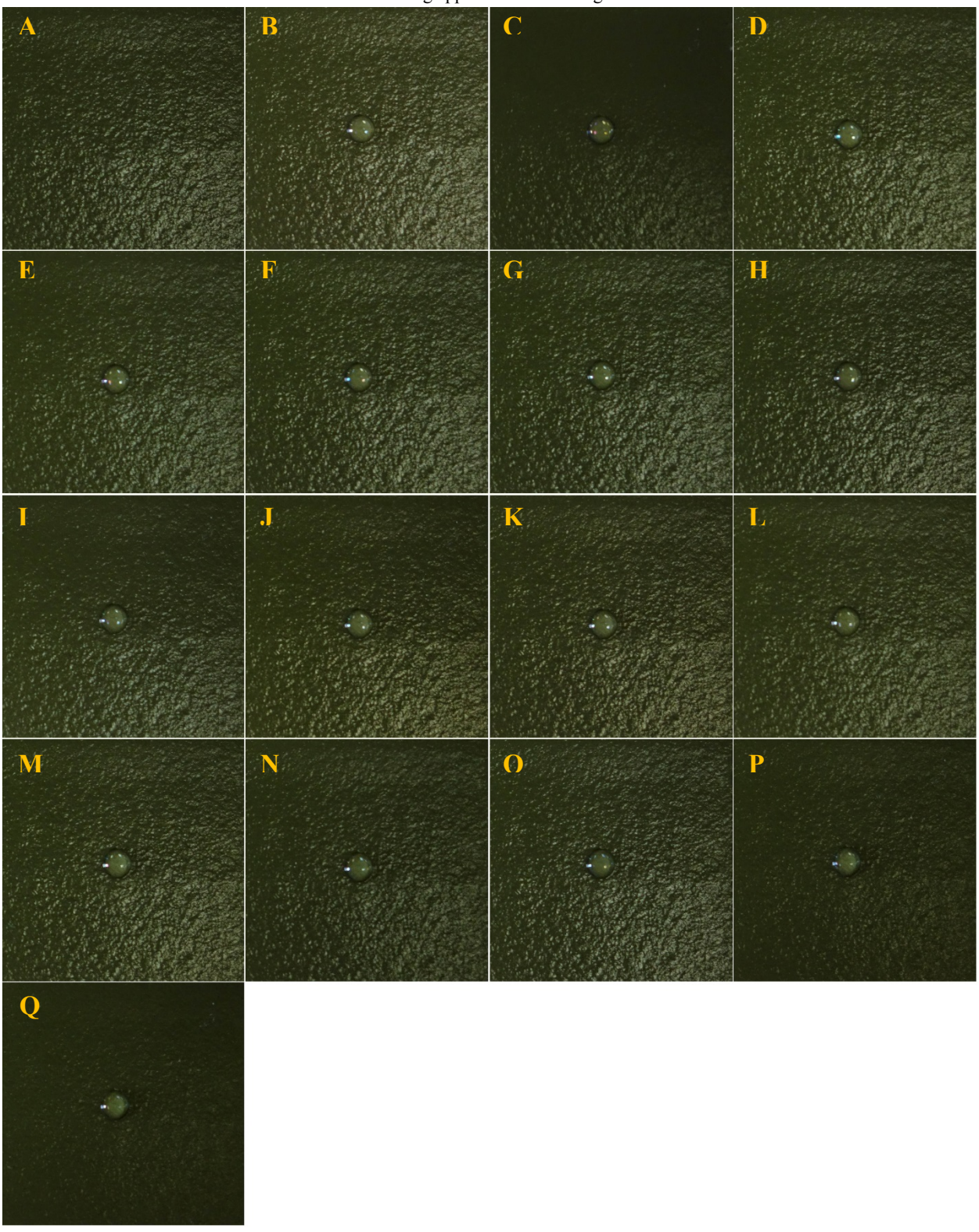

Fig. A6 — DMMP on the as synthesized SLIPS coating lubricated with Fomblin Y. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

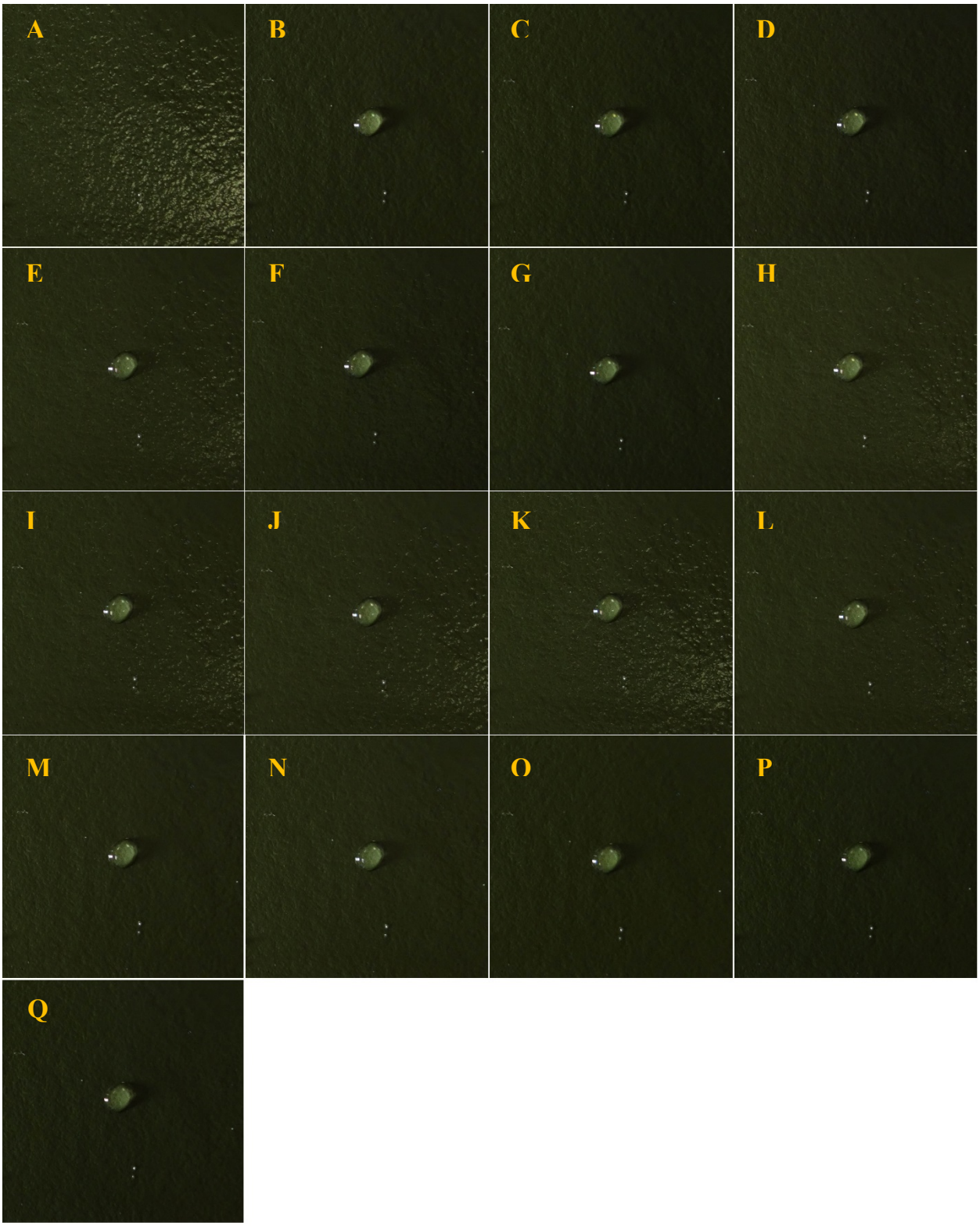

Fig. A7 — DFP on the extracted SLIPS coating lubricated with Fomblin Y. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

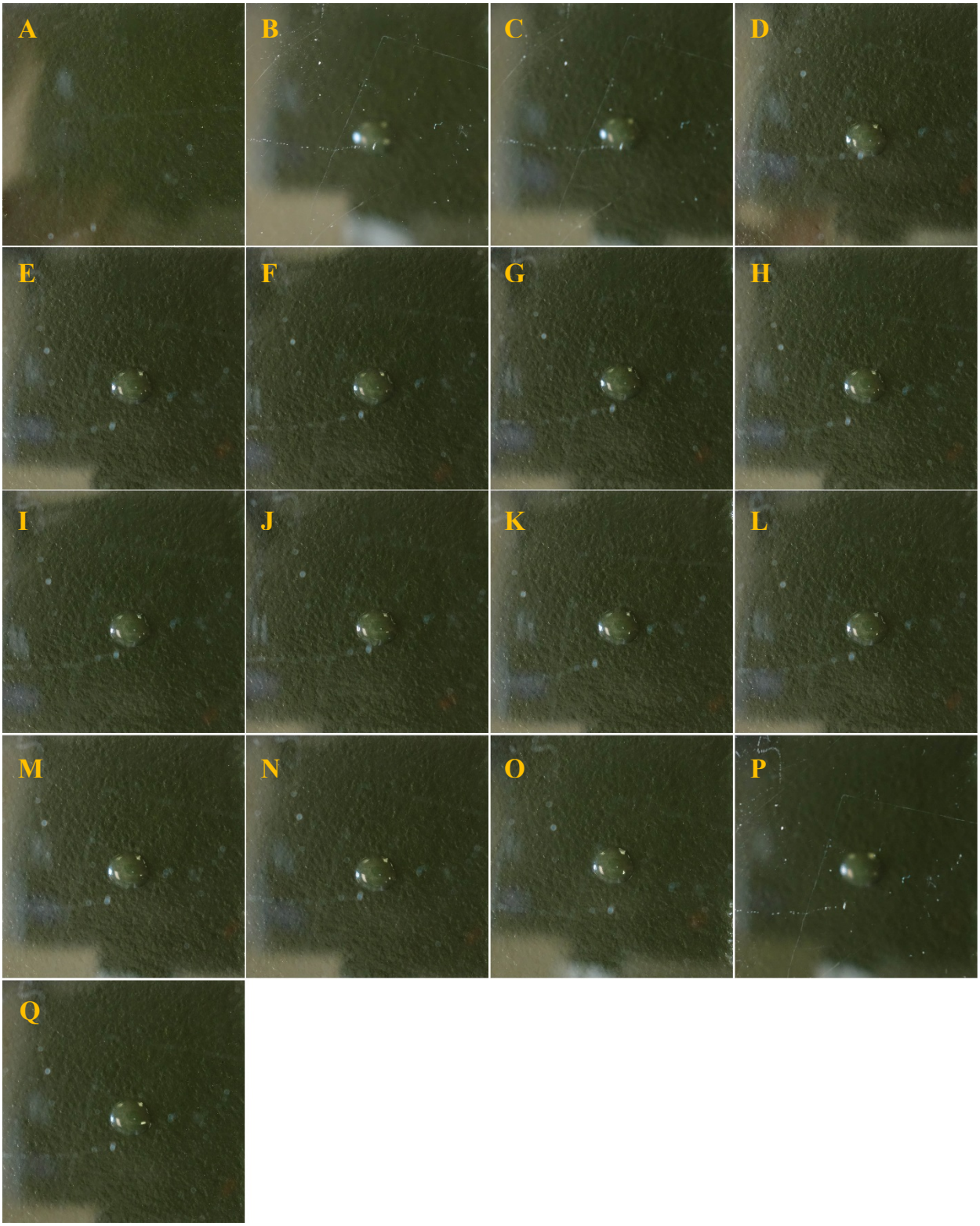

Fig. A8 — MES on the extracted SLIPS coating lubricated with Fomblin Y. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

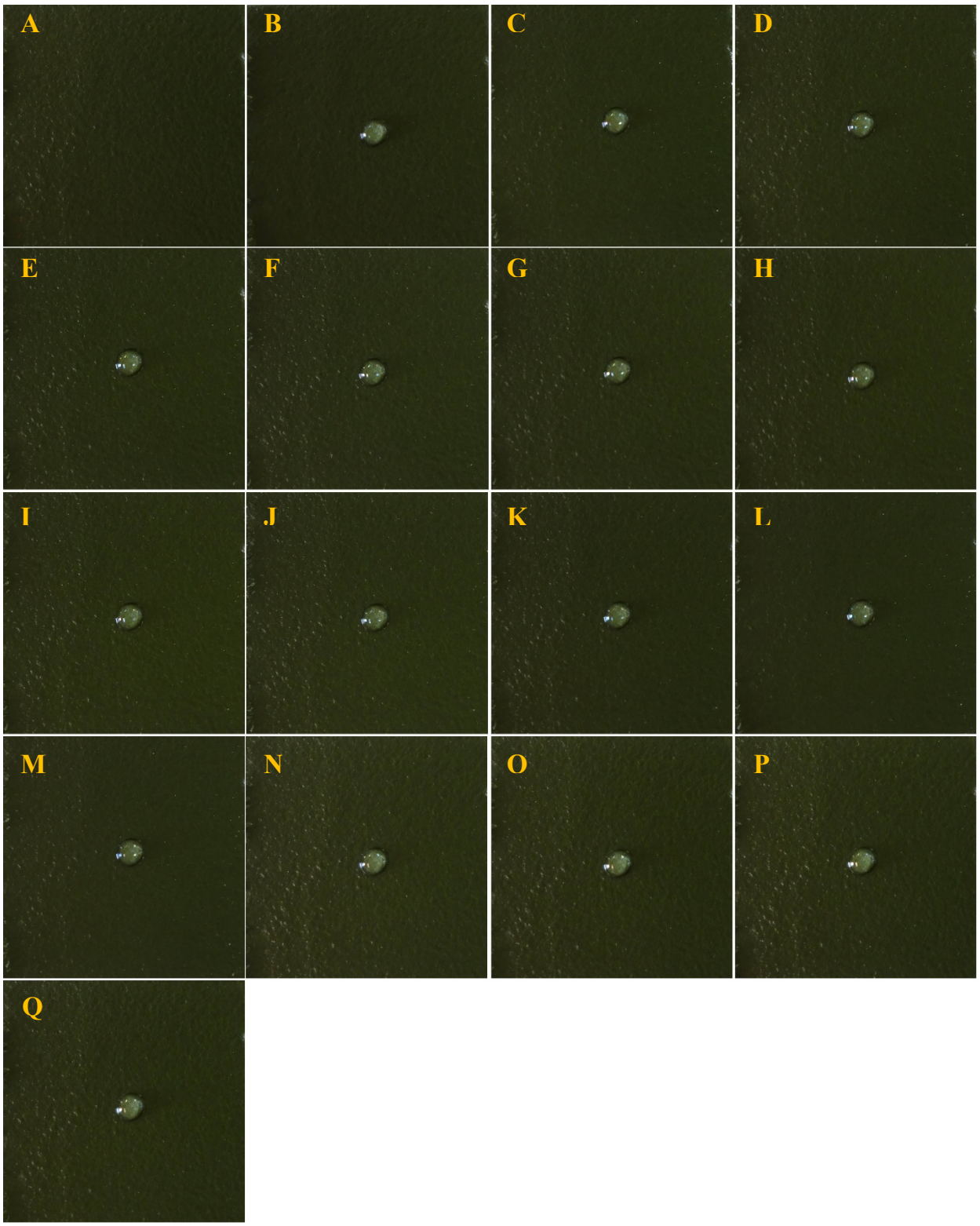

Fig. A9 — DMMP on the extracted SLIPS coating lubricated with Fomblin Y. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.